

USE OF RHODIUM-CROSSLINKING SILICONE ELASTOMERS FOR PRODUCING BAKING MOLDS

BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The invention relates to shaped bodies.

2. Background Art

 Shaped bodies, such as casting molds for the confectionary/patisserie industry, food molds, for example for shaping butter, chocolate, chocolate candies and ice cream, baking molds and baking sheets, all in general called baking molds
10 below, even if not explicitly used for baking, are well known and are generally produced from aluminum, cast iron, clay, porcelain or glass. The use of such baking molds has the considerable disadvantage that removing the foods, called baked goods below, from the baking mold is difficult, since the baking molds are rigid and immovable.

15 As an improvement, therefore, in some cases complicated baking molds have been developed which need to be opened via a mechanism, thus facilitating removal of the baked goods. Such molds are not optimal, however, since firstly a complicated mechanism is necessary, and secondly only very specific geometries of the baking molds are possible. EP 0 992 195 B1 describes the use of
20 silicone which is obtained by a platinum crosslinking process for producing patisserie molds and baking sheets. Advantages with respect to the abovementioned baking molds with this process are that the silicone is elastic and thus the baked good may be removed very easily from the baking mold, especially since the adhesion of the baked good to the silicone baking mold is extremely low, due to the
25 nature of the silicone. Other advantages are that the silicone is inert toward foods and is considered to be physiologically harmless. Furthermore, silicone can be

washed readily and has good physical and chemical resistance to oxygen, UV radiation and ozone. The same advantages also apply to food molds in general, for instance for shaping butter, chocolate/chocolate candies and ice cream, where, in addition, the advantage of the cold flexibility of silicone elastomers becomes
5 important.

Disadvantages of silicones which are crosslinked by platinum are the yellow and/or brown discoloration of the crosslinked silicones which are visible, in particular, in the case of high-volume silicone pieces. The discolorations are caused by the platinum which, at the end of the crosslinking, is present as platinum colloid,
10 as described in *J.Am.Chem.Soc.* 108 (1986) 7228ff. Furthermore, in many platinum-crosslinked silicones, transparency is decreased and the silicone elastomers are thus not transparent, but cloudy or "translucent."

The platinum catalysts have the further disadvantage that silicone rubbers which contain them have, after all the essential constituents have been mixed, only a limited processing time, since crosslinking proceeds even at room
15 temperature. Although the processing time of the compositions may be increased by incorporating substances which inhibit the activity of the platinum catalyst ("inhibitors"), their use in turn reduces the curing rate of the composition.

It would be desirable to provide shaped bodies of addition-
20 crosslinking silicones which do not have the abovementioned disadvantages.

SUMMARY OF THE INVENTION

It has now surprisingly been found that when silicones are used which are crosslinked with rhodium and/or iridium compounds instead of with platinum, above-described disadvantages and problems do not occur.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

The present invention relates to shaped bodies obtainable by addition-crosslinked silicone elastomers in the presence of at least one rhodium or iridium catalyst or mixtures of both types of catalysts.

5 The use of silicone elastomers which crosslink via rhodium and/or iridium catalysis is distinguished by the fact that the advantages of the silicones as described in the introduction are unrestricted and, in addition, the resulting silicone elastomers are extremely transparent, display no discolorations and, even without
10 than platinum-catalyzed systems, without adversely affecting crosslinking at elevated temperatures.

The silicone compositions which can be crosslinked by rhodium and/or iridium catalysts are preferably composed of the following constituents:

15 (A) at least one polydiorganosiloxane having at least one unsaturated group comprising chemically bound structural units of the formula (1)



20 (B) at least one polyorganosiloxane containing at least two Si-bound hydrogen atoms comprising chemically bound structural units of the formula (II)



and

(C) at least one rhodium catalyst and/or iridium catalyst which catalyzes the hydrosilylation reaction between (A) and (B),

where

- R independently are unsubstituted or substituted ("optionally substituted") organic hydrocarbon radicals having up to 18 carbon atoms and are free of aliphatic carbon-carbon multiple bonds,
- 5 R¹ are monovalent, optionally substituted hydrocarbon radicals having 2 to 14 carbon atoms, and have an aliphatic carbon-carbon multiple bond (double bond or triple bond), optionally bound to the silicon atom via an organic divalent linking group,
- a is 0, 1, 2 or 3,
- 10 b is 0, 1 or 2,
- with the proviso that the sum of a + b is less than or equal to 3 and on average at least 2 radicals R¹ are present per molecule,
- c is 0, 1, 2 or 3 and
- d is 0, 1 or 2,
- 15 with the proviso that the sum of c + d is less than or equal to 3 and on average at least two Si-bound hydrogen atoms are present per molecule.

Examples of radicals R include alkyl radicals such as the methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, isopentyl, neopentyl, and tert-pentyl radicals, hexyl radicals such as the n-hexyl radical, heptyl radicals such as the n-heptyl radical, octyl radicals such as the n-octyl radical and isooctyl radicals such as the 2,2,4-trimethylpentyl radical, nonyl radicals such as the n-nonyl radical, decyl radicals such as the n-decyl radical, dodecyl radicals such as the n-dodecyl radical, and octadecyl radicals such as the n-octadecyl radical, cycloalkyl radicals such as cyclopentyl, cyclohexyl, cycloheptyl and methylcyclohexyl radicals, aryl radicals such as the phenyl, naphthyl, anthryl and phenanthryl radicals, alkaryl radicals such as o-, m-, and p-tolyl radicals, xylyl radicals and ethylphenyl radicals, and aralkyl radicals such as the benzyl radical and the α - and β -phenylethyl radicals.

Examples of substituted radicals R are haloalkyl radicals such as the 30 3,3,3-trifluoro-n-propyl radical, the 2,2,2,2',2',2'-hexafluoroisopropyl radical, and

the heptafluoroisopropyl radical, and haloaryl radicals such as the o-, — and p-chlorophenyl radicals.

Preferably, radical R is a monovalent SiC-bound, optionally substituted hydrocarbon radical having 1 to 18 carbon atoms that is free from aliphatic carbon-carbon multiple bonds, more preferably a monovalent SiC-bound hydrocarbon radical having 1 to 6 carbon atoms that is free from aliphatic carbon-carbon multiple bonds, and in particular, a methyl or phenyl radical.

Radical R¹ may be any group able to participate in an addition reaction with an SiH-functional compound (hydrosilylation). Preferably, radical R¹ is an alkenyl or alkynyl group having 2 to 16 carbon atoms, such as a vinyl, allyl, methallyl, 1-propenyl, 5-hexenyl, ethynyl, butadienyl, hexadienyl, cyclopentenyl, cyclopentadienyl, cyclohexenyl, vinylcyclohexylethyl, divinylcyclohexylethyl, norbornenyl, vinylphenyl or styryl radical, or a substituted radical such as an allyloxy or vinyloxy radical, with vinyl, allyl and hexenyl radicals being particularly preferred.

The molecular weight of constituent (A) can vary within broad ranges, for instance between 10² and 10⁶ g/mol. Thus, the constituent (A) may be, for example, a relatively low molecular weight alkenyl-functional oligosiloxane such as 1,2-divinyltetramethyldisiloxane, but may also be a highly polymeric polydimethylsiloxane having chain or terminal Si-bonded vinyl groups, for example one having a molecular weight of 10⁵ g/mol (number average, determined by NMR). The structure of the molecules forming constituent (A) is also not fixed; in particular, the structure of a higher-molecular-weight, e.g. oligomeric or polymeric siloxane, can be linear, cyclic, branched or resin- or network-like. Linear and cyclic polysiloxanes are preferably composed of units of the formula R₃SiO_{1/2}, R¹R₂SiO_{1/2}, R¹RSiO_{2/2} and R₂SiO_{2/2}, where R and R¹ have the meaning specified above. Branched and network-like polysiloxanes additionally contain trifunctional and/or tetrafunctional units, those of the formulae RSiO_{3/2}, R¹SiO_{3/2} and SiO_{4/2} being preferred. Obviously, mixtures of different siloxanes satisfying the criteria of the constituent (A) can also be used. Particular preference as to component (A) is given

to the use of vinyl-functional, substantially linear polydiorganosiloxanes having a viscosity of 0.01 to 100,000 Pa·s, more preferably 0.1 to 30,000 Pa·s, in each case at 25°C.

5 As organosilicon constituent (B), all hydrogen-functional organosilicon compounds which have a viscosity of 1 to 100,000 mPa·s, preferably 10 to 10,000 mPa·s, and preferably 50 to 1000 mPa·s, in each case at 25°C, which are useful in addition-crosslinkable compositions may be used. Preferably, the organopolysiloxane (B) contains Si-bonded hydrogen in the range from 0.04 to 1.7 percent by weight, based on the total weight of the organopolysiloxane (B).

10 The molecular weight of the constituent (B) can likewise vary within broad limits, for instance between 10^2 and 10^6 g/mol. Thus, the constituent (B) may be, for example, a relatively low-molecular-weight SiH-functional oligosiloxane, such as tetramethyldisiloxane, but may also be a highly polymeric polydimethylsiloxane having chain or terminal SiH groups, or a silicone resin having SiH groups.

15 The structure of the molecules forming the constituent (B) is also not fixed; in particular the structure of a higher-molecular-weight, e.g. oligomeric or polymeric SiH-containing siloxane can be linear, cyclic, branched, or else resin- or network-like. Linear and cyclic polysiloxanes are preferably composed of units of the formula $R_3SiO_{1/2}$, $HR_2SiO_{1/2}$, $HRSiO_{2/2}$ and $R_2SiO_{2/2}$, where R has the meaning

20 specified above. Branched and network-like polysiloxanes additionally contain trifunctional and/or tetrafunctional units, those of the formulae $RSiO_{3/2}$, $HSiO_{3/2}$ and $SiO_{4/2}$ being preferred. Obviously, mixtures of different siloxanes satisfying the criteria of the constituent (B) can also be used. In particular, the molecules forming the constituent (B), in addition to the obligatory SiH groups, may also at the same

25 time contain aliphatically unsaturated groups. Particular preference is given to the use of low-molecular-weight SiH-functional compounds, such as tetrakis(dimethylsiloxy)silane and tetramethylcyclotetrasiloxane, and also higher-molecular-weight, SiH-containing siloxanes, such as poly(hydrogenmethyl)siloxane and poly(dimethylhydrogenmethyl)siloxane having a viscosity at 25°C of 10 to

30 10,000 mPa·s, or analogous SiH-containing compounds in which a portion of the methyl groups is replaced by 3,3,3-trifluoropropyl or phenyl groups.

Constituent (B) is preferably present in the inventive crosslinkable overall silicone compositions in such an amount that the molar ratio of SiH groups to aliphatically unsaturated groups is 0.1 to 20, more preferably between 0.7 and 5.0. The components (A) and (B) used are commercially available products or can
5 be prepared by processes customary in organosilicon chemistry.

Examples of component (C) include rhodium compounds such as $[\text{Rh}(\text{O}_2\text{CCH}_3)_2]_2$, $\text{Rh}(\text{O}_2\text{CCH}_3)_3$, $\text{Rh}_2(\text{C}_8\text{H}_{15}\text{O}_2)_4$, $\text{Rh}(\text{C}_5\text{H}_7\text{O}_2)_3$, $\text{Rh}(\text{C}_5\text{H}_7\text{O}_2)(\text{CO})_2$, $\text{Rh}(\text{CO})[\text{Ph}_3\text{P}](\text{C}_5\text{H}_7\text{O}_2)$, $\text{Rh}(\text{CO})_2(\text{C}_5\text{H}_7\text{O}_2)$, $\text{RhCl}_3[(\text{R})_2\text{S}]_3$, $(\text{R}^2_3\text{P})_2\text{Rh}(\text{CO})\text{X}$, $(\text{R}^2_3\text{P})_3\text{Rh}(\text{CO})\text{H}$ and $\text{Rh}_2\text{X}_2\text{Y}_4$, where X is hydrogen, chlorine, bromine or iodine, Y is
10 ethyl, CO, C_8H_{14} or $0.5 \text{ C}_8\text{H}_{12}$, R is as defined above and R^2 is an alkyl radical such as a methyl, ethyl and butyl radical, or an aryl radical such as phenyl and tolyl radical, or an oxygen-substituted radical such as a methoxy, ethoxy or phenoxy radical. Preferred rhodium catalysts are (acetylacetonato)carbonyl(triphenylphosphine)rhodium(I), (acetylacetonato)dicarbonylrhodium(I), carbonylchlorobis(triphenylphosphine)rhodium(I),
15 (acetylacetonato)(1,5-cyclooctadiene)rhodium(I), rhodium(II) acetate dimer, rhodium(III) acetylacetonate and rhodium(II) octanoate dimer.

Further examples for the component (C) include iridium compounds, such as $\text{Ir}(\text{OOCCH}_3)_3$, $\text{Ir}(\text{C}_5\text{H}_7\text{O}_2)_3$, $[\text{Ir}(\text{Z})(\text{En})_2]_2$ and $[\text{Ir}(\text{Z})(\text{Dien})]_2$, where Z is chlorine, bromine, iodine or alkoxy, En is olefin such as ethylene, propylene,
20 butene, cyclohexene or cyclooctene, and Dien is cyclooctadiene. Preferred iridium catalysts are chlorobis(cyclooctane)iridium(I) dimer, chlorobis(1,5-cyclooctadiene)iridium(I) dimer and iridium(III) acetylacetonate.

The amount of component (C) used depends on the desired crosslinking rate and on the respective use and also on economic aspects. The
25 compositions preferably contain component (C) in amounts such that a metal content of 0.05 to 500 ppm by weight (parts by weight of metal per million parts by weight of silicone composition), more preferably 0.5 to 100 ppm by weight, and in particular 1 to 50 ppm by weight, results.

The inventive shaped bodies of silicone elastomer can optionally contain, as constituent (D), other additives, including those which have customarily been used in silicone elastomers, at a content of up to 70% by weight, preferably 0.0001 to 40% by weight. These additives can be, for example, active fillers, such as hydrophobic and hydrophilic silicas, inactive fillers, resin-like polyorganosiloxanes which are different from the siloxanes (A) and (B), dispersion aids, solvents, adhesion promoters, coloring agents such as inorganic pigments (for example cobalt blue) and organic dyes, plasticizers, organic polymers, inhibitors, stabilizers etc. These include additives such as silica flour, diatomaceous earth, clays, chalk, lithophone, soots, graphite, metal oxides, metal carbonates, metal sulfates, metal salts of carboxylic acids, metal dusts, fibers such as glass fibers, plastic fibers, plastic powder, dyes, pigments etc. In addition, compounds can be added for improving the heat stability and flame retardancy, i.e. "heat stabilizers." All stabilizers, including those previously used in silicone rubbers, may be used. Preferably, however, the heat stabilizers are transition metal compounds and soot. Preferred examples include cerium oxide, cerium octoate, cerium-siloxane compounds, iron oxide, iron octoate, iron-siloxane compounds, zinc carbonate, manganese carbonate and titanium oxide.

Examples of reinforcing fillers are preferably pyrogenic or precipitated silicas having BET surface areas of at least 50 m²/g, and soots and activated carbons such as furnace soot and acetylene soot, pyrogenic and precipitated silicas having BET surface areas of at least 50 m²/g being preferred. The silica fillers can have a hydrophilic character or can be made hydrophobic by known processes. When hydrophilic fillers are added, the addition of a hydrophobicizing agent is necessary. In addition, there can be present additives (D) which serve for the targeted setting of the processing time, kick-off temperature and crosslinking rate of the inventive compositions. These inhibitors and stabilizers are very well known in the field of addition-crosslinking compositions. Examples of customary inhibitors are acetylenic alcohols such as 1-ethynyl-1-cyclohexanol, 2-methyl-3-butyn-2-ol, 3,5-dimethyl-1-hexyn-3-ol and 3-methyl-1-dodecyn-3-ol; polymethylvinylcyclsiloxanes such as 1,3,5,7-tetravinyl-tetramethyltetracyclosiloxane; low-molecular-weight silicone oils containing

5 methylvinylSiO_{2/2} groups and/or R₂vinylSiO_{1/2} terminal groups such as divinyltetramethyldisiloxane, and tetravinyl dimethyldisiloxane; trialkyl cyanurates; alkyl maleates such as diallyl maleates, dimethyl maleate and diethyl maleate; alkyl fumarates such as diallyl fumarate and diethyl fumarate; organic hydroperoxides
10 such as cumene hydroperoxide, tert-butylhydroperoxide and pinane hydroperoxide; organic peroxides; organic sulfoxides; organic amines, diamines and amides; phosphines and phosphites; nitriles; triazoles; diaziridines; and oximes. The effect of these inhibitor additions depends on their chemical structure, so that they need to be determined individually. The inhibitor content, however, is preferably 0 to 50,000 ppm, more preferably 0 to 1000 ppm, and in particular, 0 to 100 ppm.

15 The inventive shaped bodies are prepared in such a manner that the constituents (A), (B), (C) and optionally constituents (D) are mixed and then crosslinked, preferably at 80 to 220°C, more preferably 150 to 190°C, in a heated casting mold, injection mold, compression mold or transfer mold. The crosslinking
time for the shaped bodies depends on the geometry of the mold and the wall thickness of the shaped bodies, for example a baking mold, and is preferably between 10 sec and 5 min. The silicone baking mold is then heated in an oven with a supply of air at a maximum temperature of approximately 200°C for 4 hours.

20 The inventive shaped bodies are preferably electronic components, diving goggles, pacifiers, spectacle pads, any adhesions and coatings with transparent substrates, such as glass and polycarbonate, tubes, profiles, seals and damping elements, etc. Preference is given to food molds, such as baking molds or molds for producing confectionery products such as chocolates.

25 Advantages of the silicone elastomers which are produced by addition crosslinking in the presence of rhodium compounds and/or iridium compounds for producing baking molds are:

- 1) Free choice of geometry of the mold, preferably a baking mold, thick rear sections being possible;

- 2) A glassy transparency making possible direct visual (noninvasive) inspection of the baked good;
- 3) No yellow and/or brown discoloration of the crosslinked silicone elastomers;
- 5 4) Processing time being decidedly long even without use of inhibitors; and
- 5) Very rapid crosslinking at elevated temperatures.

Points 3) and 4) make it possible for the processor to have a great deal of play in the processing.

10 Example 1

A laboratory kneader was charged with 405 parts of a vinyl dimethylsiloxy-terminated polydimethylsiloxane having a viscosity of 20 Pa·s. Following heating to 150°C, 366 parts of a hydrophobic pyrogenic silica having a specific BET surface area of 300 m²/g and a carbon content of 4.2% by weight were
15 added, producing a high-viscosity composition which was then diluted with 229 parts of the abovementioned polydimethylsiloxane. By kneading under vacuum (10 mbar) at 150°C, volatile constituents were removed in the course of one hour. This composition is termed base composition 1.

Component A

20 906 parts of the base composition 1 were mixed homogeneously under vacuum in a kneader at room temperature with 7 parts of a vinyl dimethylsiloxy-terminated polydimethylsiloxane having a viscosity of 20 Pa·s and 0.061 parts of bis(triphenylphosphine)carbonylrhodium(I) chloride, corresponding to 10 ppm of rhodium in the total mass of component A, dissolved
25 in tetrahydrofuran.

Component B

931 parts of the base composition 1 were mixed on a roller at a temperature of 25°C with 55 parts of SiH crosslinker to give a homogeneous composition. The SiH crosslinker was a trimethylsiloxy-terminal methylhydrogenpolysiloxane, $\text{Me}_3\text{Si}-(\text{-O-SiH(Me)})_n\text{-O-SiMe}_3$, which according to ^{29}Si -NMR has a number average chain length of $n=53$.

Before crosslinking, the components A and B were mixed in a ratio of 1:1 using a laboratory agitator.

Example 2

Similar to Example 1, except that instead of the bis-(triphenylphosphine)carbonylrhodium(I) chloride/tetrahydrofuran solution, 0.029 parts of rhodium(III) acetylacetonate dissolved in dichloromethane were used.

Example 3

Similar to Example 1, except that instead of bis(triphenylphosphine)carbonylrhodium(I) chloride/tetrahydrofuran solution, 0.021 parts of carbonyltriphenylphosphinerhodium(I) acetylacetonate dissolved in dichloromethane were used.

Comparative Example 1

The procedure described in Example 1 is repeated except that the catalyst used was 16 ppm of platinum as platinum-divinyltetramethyldisiloxane complex in vinyl-terminated polydimethylsiloxane (commercially available from ABCR GmbH & Co, Germany).

Comparative Example 2

The procedure described in Example 1 is repeated except that the catalyst used was 16 ppm of platinum as platinum-divinyltetramethyldisiloxane complex in vinyl-terminated polydimethylsiloxane (commercially available from
5 ABCR GmbH & Co, Germany) and 2 parts of ethynylcyclohexanol were used as inhibitor.

Example 4

589.4 parts of a vinyl dimethylsiloxyl-terminated polydimethylsiloxane having a Brabender plasticity of 630 mkp equivalent to a mean molar mass of
10 approximately 500,000 g/mol were mixed with 252.6 parts by mass of a hydrophobic pyrogenic silica having a BET surface area of 300 m²/g and a carbon content of 3.95% by weight, which were added in portions, for 4 hours in a kneader to provide a homogeneous composition, base composition 2.

500 parts of base composition 2 were mixed on a roller at a
15 temperature of 20°C with 0.1 part of inhibitor, 7.5 parts of SiH crosslinker and 2 parts of catalyst batch to give a homogeneous composition, in which the inhibitor used was 1-ethynyl-1-cyclohexanol, and the SiH crosslinker was a mixed polymer of dimethylsiloxyl, methylhydrogensiloxyl, and trimethylsiloxyl units having a viscosity of 310 mPa·s at 25°C and a Si-bonded hydrogen content of 0.46% by
20 weight. The catalyst batch is prepared by homogenizing 200 parts of base composition 2 with 1.8 parts of rhodium(II) octanoate dimer (dissolved in dichloromethane) for 30 minutes in a kneader.

Comparative Example 3

The procedure described in Example 4 is repeated except that the
25 catalyst used was 10 ppm of platinum as platinum-divinyltetramethyldisiloxane complex in vinyl-terminated polydimethylsiloxane (commercially available from

ABCR GmbH & Co, Germany) and 0.5 parts of 1-ethynyl-1-cyclohexanol inhibitor were used.

The thermal curing properties of the silicone compositions prepared in Examples 1 to 4 and Comparative Examples 1 to 3 (C1, C2, C3) were measured using a Goettfert Elastograph, 7 hours after the A and B components had been mixed in a ratio of 1:1. Example 4 and Comparative Example 3 were measured immediately after mixing.

For quantitative determination of the stability, the formulations prepared were stored at room temperature (RT), the time (measured in days) for the initial viscosity value to double being determined. The measurement results are shown in Table 1.

Table 1:

Examples	1	2	3	C1	C2	4	C3
a_T [°C]	132	125	118	-*	120	135	122
Storage at RT	> 10 d	> 10 d	> 10 d	< < 1 d	< 8 d	> 10 d	< 4 d

-*: The mixture was already crosslinked before measurement.

d: days

s: seconds

The kick-off temperature a_T was determined at a heating rate of 10°C/min. The temperature corresponding to the 4% value of maximum torque was defined as the kick-off temperature. The t_{50} value was determined in accordance with DIN 53529 T3. The time from the start of curing to 50% (t_{50} value) of the maximum torque was determined at 150°C.

For further comparison, crosslinked silicone rubber films were produced from the silicone compositions and the mechanical properties were determined. The crosslinked silicone rubbers were produced by crosslinking the mixtures of the respective examples in a hydraulic press at a temperature of 170°C for 10 minutes to give the silicone rubber. The demolded silicone rubber films approximately 2 mm or 6 mm thick were subjected to mechanical tests. The result can be taken from Table 2.

Table 2:

	Hardness [Shore A]	RF [N/mm ²]	RD [%]	Appearance
Example 1	58	11.8	570	colorless, transparent
Example 2	56	10.4	550	colorless, transparent
Example 3	60	11.0	580	colorless, transparent
Comparison C1	_*	_*	_*	_*
Comparison C2	60	10.8	580	slight yellow discoloration
Example 4	37	12.3	1180	colorless, transparent
Comparison C3	39	13.0	1100	yellow stain

_* Already crosslinked in advance.

Hardness: Shore A hardness determined in accordance with DIN 53505,

RF: Tear strength determined in accordance with DIN 53504-S1

RD: Elongation at break determined in accordance with DIN 53504-S1

While embodiments of the invention have been illustrated and described, it is not intended that these embodiments illustrate and describe all possible forms of the invention. Rather, the words used in the specification are words of description rather than limitation, and it is understood that various changes may be made without departing from the spirit and scope of the invention.